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Chapter

Morphology Controlled Synthesis of the Nanostructured Gold by Electrodeposition Techniques

Brij Mohan Mundotiya and Wahdat Ullah

Abstract

The gold nanostructures find several technological applications in MEMS, optoelectronics, and electronics industries. To enhance the applicability and suitability of the gold nanostructures in these fields, modification of the morphology of the deposited nanostructure is required. In recent years, the electrodeposition method has emerged as a widely known method for the deposition of the nanostructures of different dimensions and morphologies due to its time efficiency, cost-effectiveness, and absence of vacuum technology. In this method, the morphology of the deposited gold nanostructure can also be easily controlled by tuning the electrodeposition process parameters such as electrolyte concentration, electrolyte temperature, current density, deposition time, etc. This chapter gives a detailed overview of the crucial electrodeposition parameters affecting the morphology of the gold nanostructures deposits.

Keywords: deposition parameters, electrodeposition, electrolyte, morphology, nanostructured gold, stability

1. Introduction

The origin of the word gold comes from the old English Anglo-Saxon word for geolo meaning "yellow", while the symbol 'Au' of gold is originated from the Latin word aurum, meaning 'shining dawn' [1]. Gold is a precious element and has an atomic number 79. In nature, it exists in a pure form. It is lustrous, slightly reddish yellow in color, soft, has high density, high corrosion resistance, highly malleable and ductile. Due to these properties, it has a long history in playing a very important role in the development of human societies since ancient time to till date. It was used by Chinese and Egyptians in ancient time (in the fifth or fourth century B.C). Gold is used in both bulk and nanostructure forms. In bulk form, gold is used in making jewelry, coins, statues, decorative objects, etc. Nanostructured gold materials are not new materials for mankind. Gold materials with nanostructures were used by mankind since a long time, but due to unavailability of characterizing tools for nanostructure (like high-resolution transmission electron microscopy (HRTEM), atomic force microscopy (AFM), X-ray diffractometer (XRD), etc.) their structures were unrevealed. Nanostructured gold is used in the microelectromechanical system (MEMS) due to its properties of high electrical conductivity, excellent corrosion resistance, solderability, thermal conductivity, and bondability.

For applications of nanostructured gold coating in MEMS, the coating must have some essential basic properties which are as follows [2]: (a) Conductivity of coating should be high; (b) Adhesion should be strong between coating and substrate to prevent cracking, delamination and spallation; (c) Residual stress in the coating should be minimum; (d) Coating should be stable within a wide range of temperature; and (e) Coating should also be resistant to surface wears, corrosion, and oxidation. Gold has also a good combination of high electrical conductivity and corrosion resistance; therefore, it is widely used as a standard material for interconnections, bond pads, contacts, as well as conductors, electrodes, and other passive components [3]. For the electrical connectors and contacts, deposit of gold has high hardness and good wear resistant [4]. Nanostructured gold also used in a variable capacitor, chemical and biological sensors, optical detectors, etc. [2].

Electrodeposition technique is a well-established versatile technique to synthesize nanostructured gold on the conducting substrate. The earliest reference to the gold coating by the electrodeposition process can be found in 1805 [1]. Relative to other deposition techniques like sputtering [5], evaporation [6] and molecular beam epitaxy [7], electrodeposition technique has many advantages such as time efficiency, low cost, high deposition rate, relatively inexpensive equipment due to absence of vacuum technology, thickness and uniformity controllable of the layers of the deposited coatings, etc. The properties of the deposited nanostructured gold coating are simply controlled by tuning its morphology. And, the morphology of the deposited gold can be tuned by changing the electrodeposition process parameters; mainly in the composition and pH of the electrolyte, the magnitude of the applied current density, temperature of electrolyte and substrate. Moreover, it is also found that the addition of some suitable additive in the electrolyte and a pretreatment of the conductive substrate can also modify the morphology of deposited gold [8]. It is also reported by Tian et al. [9] that the variation in the applied potential to the electrodes and concentration of the precursor gold in the electrolyte plays a very crucial role in modification of the geometries and morphologies of the gold deposits. On the variation of applied potential to the electrodes, they obtained pyramidal, rod-like, and spherical morphologies of nanostructured gold in a pre-treated substrate.

In this chapter, an overview of the information related to effects of process parameters in the morphologies of nanostructured gold deposits is provided in detail.

2. Electrodeposition of gold

Schematic of the electrodeposition process is shown in **Figure 1**. For the electrodeposition process, an electrolytic cell, an electrolyte, electrodes (an anode and a cathode), and a power supply source are required. The electrolyte is the electrochemical solution of metal or alloy salts that is/are required to deposit at cathode (conductive substrate) surface during electrolysis. When a power source is connected to the terminals of electrodes, the current flows through them. As a result of this, the cations (the metal ions (M^{Z+})) are attracted to the cathode and deposited on it. The continuous deposition of metal ions on the cathode surface forms a uniform layer of metal on it through the reduction process. During the electrodeposition process, following chemical reactions (Eqs. (1) and (2)) take place at cathode and anode:

$$Cathode: \quad M^{Z+} + Ze^{-} \rightarrow M \tag{1}$$

$$Anode: \quad M \rightarrow M^{Z+} + Ze^{-} \tag{2}$$

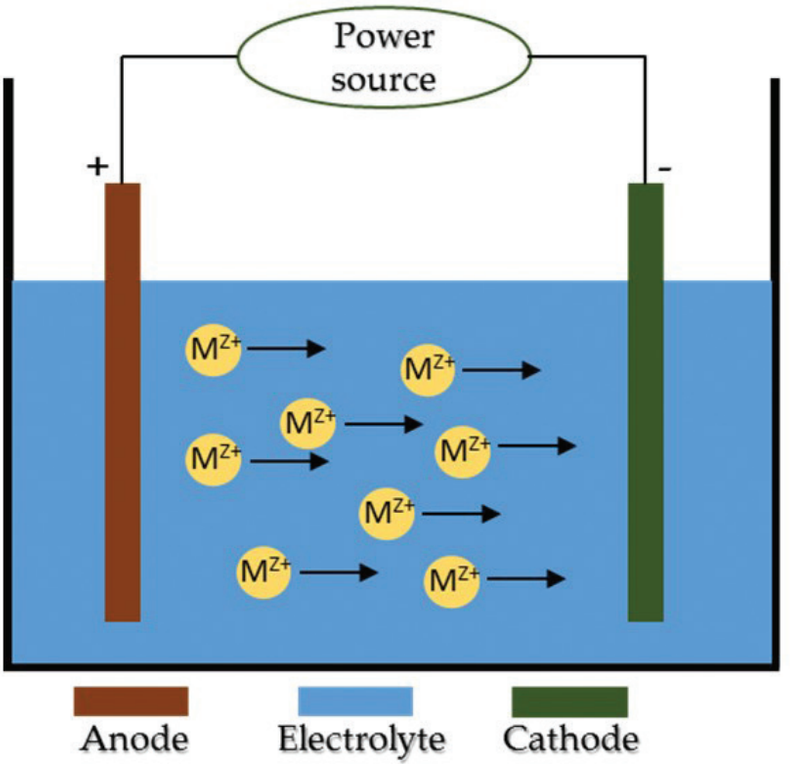

Figure 1.
Schematic of an electrodeposition process.

In electrodeposition of metal or metal alloy, according to requirement one can use two types of anodes: (a) sacrificial anode and (b) permanent anode. The sacrificial anode is a dissolvable anode and it is made up of metal being deposited on the cathode. During electrodeposition process, sacrificial anode sacrifices itself and provides the metal ions to the electrolyte. On the other hand, permanent anode or inert anode is generally made of platinum and carbon. This type of anode is employed only to complete the electrical circuit. It does not give any metal ions to the electrolyte during electrodeposition process. The cathode is the substrate on that deposition is carried out.

Electrolytes used for deposition of gold nanostructures are generally cyanide and noncyanide based. Gold is present in these electrolytes primarily in the oxidation states like +1 and +3. The $[Au(CN)_2]^-$ is the most commonly used gold complex for the deposition of gold. This complex has the stability constant of 10^{39} and the oxidation state of +1. One more frequently used gold complex is anionic chlorocomplex $[AuCl_4]^-$ in hydrochloric solution which exists in the +3 oxidation state. The other popular complexes of gold are gold sulfite $[Au(SO_3)_2]^{-3}$ and gold thiosulfate $[Au(S_2O_3)_2]^{-3}$. Stability constant of gold sulfite and gold thiosulfate are 10^{10} and 10^{28}, respectively [1].

Most of the electrodeposited gold coatings have some degree of compressive/tensile residual stresses. The residual stress of gold coating is unwanted for its application in the MEMS. Because the residual stresses create curvatures in the coating which provide the most prone sites for creation of nano/microcracks. Also, chances of delamination of the coating from the substrate increases due to the presence of residual stresses on it. Presence of high level of residual stresses in the gold coatings also leads the risk of breakage of the wafer during handling. Therefore, minimization of residual stresses in the electrodeposited coating is an essential requirement for its application in the fabrication of coating based devices. It is found that the residual stresses in deposited coatings can be controlled by changing the electrodeposition process parameters. It has been reported in scientific literature that the

developed residual stresses in electrodeposited coatings are the function of current density [10–12], electrolyte temperature [12], coating thickness [10], cathode agitation [4], and brighteners [12]. The developed stress in the deposited coatings can be calculated by using the Stoney's formula for thin film. For this purpose, the wafer curvature before and after the deposition is measured by using a profilometer. The load and scanning speed is kept fixed during the curvature measurement. Stress in the film is expressed by Stoney's formula given in Eq. (3) [13]:

$$\sigma_f = \frac{E_s h_s^2 k}{6 h_f (1 - \nu_s)} \tag{3}$$

where σ_f is the stress in the coating, h_f is the thickness of the coating, h_S thickness of the substrate, E_S is Young's modulus of the substrate, k is the curvature difference between the coating and substrate, and ν_s is the Poisson's ratio.

Normally, two types of electrodeposition methods for deposition of gold nanostructures, namely: (a) DC electrodeposition and (b) pulse electrodeposition. In this chapter, we will be focused on DC electrodeposition method for deposition of gold nanostructures.

3. Gold electrodeposition solution

As the gold is one of the costliest metal, therefore, it is necessary to identify the best and suitable electrolyte solution to reduce the deposition cost of the desirable gold nanostructures by electrodeposition. The first trace of deposition of gold onto the silver substrate by the electrodeposition process can be found in work of Italian chemist Luigi Brugnatelli in 1805 [1]. A wide range of suitable electrolytes for deposition of gold with nanostructures have been identified by researchers so far (see **Table 1**). For the deposition of nanostructured gold, the electrolyte baths have been classified into different classes such as cyanide-based and noncyanide-based electrolytes. Cyanide-based electrolyte could be operated at acidic (pH value less than 7), neutral (pH value equal to 7), or alkaline (pH more than 7) pH's. The deposited nanostructured gold from this electrolyte can be soft or hard. On the other hand, noncyanide-based electrolytes could be operated only at neutral or alkaline pHs. And, deposited gold by these electrolytes is soft [18]. The hardening of deposited gold occurs due to the co-deposition of gold with metals such as nickel, cobalt, and iron. The co-deposited metals such as nickel, cobalt, and iron are known as hardening agents.

Traditionally, classical cyanide-based electrolyte bath is most frequently used for the deposition of nanostructured gold. From this electrolyte bath, the deposited gold coating is either pure or may contain an impurity of some other metals such as silver, nickel, cobalt, and copper. Co-deposition of these metals in the deposited gold could alter its color. Furthermore, the cyanide-based electrolyte is highly toxic. The other problem associated with electrodeposition of gold using cyanide-based electrolytes is that they often incompatible with positive photoresist [17]. The electrolyte attacks the interface between the resist film and the substrate which leads to change in the geometry of pattern of the desired component in MEMS that created in the photoresist. The component has a different shape and size after the electrodeposition. Therefore, researchers and scientist are looking to develop an electrolyte bath that is nontoxic and compatible with microdevice manufacture such as the conventional photoresist used to delineate bump pattern.

A sulfite-based electrolyte bath is alternatively used for the deposition of the nanostructured gold in MEMS applications. Sulfite based electrolyte has been

Type	Composition	pH	Temperature (°C)	Current density (mA/cm^2)	Substrate
Dicyanoaurate bath [14]	$KAu(CN)_2$: 12 g/L Citric acid: 40 g/L NH_4-citrate: 40 g/L	–	Room temperature	<0.25	Cu
Sulfite bath [4]	Commercially solution: Metalor ECF 60	9.5	22–60	1–5	A seed layer of Au on Si-wafer
Cyanide bath [2]	Commercial solution: ATOTECH^{TM} gold potassium cyanide	–	45–75	1–7	Seed layer of Cr/Au on Si- wafer
Cyanide bath [8]	$K[Au(CN)_2]$: 10 g/L KH_2PO_4: 100 g/L	–	55	–	Transparent conductive oxide glass (glass/SnO_2:F)
Sulfite bath [15]	$Na_3Au(SO_3)_2$: 0.080 mol/L Na_2SO_3: 0.32 mol/L Tl_2SO_4: 1 mmol/L	9	23	1.5	Seed layer of Au on Si-wafer
Chloride bath [16]	$HAuCl_4$: 0.02–0.20 mmol/L	7	30	–	ITO glass
Chloride bath [9]	$HClO_4$: 0.1 M $HAuCl_4$: 4–40 mM	–	–	–	ITO glass
Sulfite bath [17]	Technigold 25E	6.5	35	1–4	Copper beryllium alloy strip

Table 1.
Electrolyte solution and some parameters of Au-electrodeposition.

known since 1842. This bath consists of gold(I) sulfite complex ($[Au(SO_3)_2]^{3-}$). However, the major issues associated with sulfite-based electrolytes are its solution solubility and instability under neutral or slightly acidic conditions necessary for optimum resist compatibility [19, 20]. Sulfite-based electrolyte bath without stabilizing agents suffers instability due to low solubility constant (10^{10}) as compared to cyanide complex, $[Au(CN)_2]^-$ which has a relatively higher stability constant, 10^{39} [1, 18]. When alkaline soluble positive resists are used in an alkaline condition (pH 8.5–10), another problem of mixing of a significant amount of contamination of organic compound in gold coatings arises. Because, in alkaline condition, the positive photoresist dissolves with a slow rate, as a result of this, contamination of organic compound is mixed with deposited gold [21]. To solve this issue, the sulfite-based electrolyte is operated preferably in the neutral or acidic medium. Stabilizing additives such as the polyamine aromatic nitro compound and 2,2′-bipyridine are used to stabilize the electrolytic bath in the neutral or acidic medium [18, 21]. The polyamine such as ethylenediamine helps to operate the electrolyte at lower pH range of 5–8. With a combination of ethylenediamine and nitrobenzene, the electrolyte bath could be operated at pH value as low as 4.0–6.5 [18].

Many cyanide and noncyanide-based electrolytes are now commercially available and actually being in the industry to synthesize nanostructure gold deposits with desired properties.

4. Electrodeposition of zero-dimensional gold nanostructures

The gold nanoparticles are used in photo-electrical accessories, biochemical sensors, electrocatalytic activity, etc. By variation of the size and density of the nanoparticles, the performance of these devices can be altered. Dolati et al. [22] produced the gold nanoparticles by using the electrolyte of chloride solution (1 mM $HAuCl_4$, 0.5 M H_2SO_4) of with cysteine additives. Cysteine (2-amino-3-mercaptopropanoic acid) is a complexing agent which provide helps to deposit the gold particles on the surface of cathode separately. Cysteine also acts as a grain refining agent in the gold nanoparticle deposition. Gold nanoparticles can also be produced by using an electrolyte of chloride solution, as reported by Zhu et al. [23]. They deposited gold nanoparticles on NH_2-reduced graphene oxide (rGo-NH_2). This modified electrode is used for the determination of adenosine triphosphate. The determination limit of these electrodeposited gold nanoparticles on rGo-NH_2 shows a range from 10 pM to 100 nM.

The morphologies of the deposited gold nanoparticles can be controlled by the deposition parameters. Zhang et al. [24] explored the influences of current densities on the sizes of the deposited gold nanoparticles. They deposited arrays of gold nanoparticles on an indium tin oxide (ITO) glass, as shown in **Figure 2**. It was observed that the particle size decreases with increasing applied current densities. Moreover, the particle densities were found to increase with increasing current density. At the current density of 5.92 mA/cm^2, the mean size of particles was about 18 nm with broader size distribution and low particle density. When the current density was decreased to 0.75 mA/cm^2, the particle size was increased with broader size distribution. At the current density to 0.3 mA/cm^2, only very few big particles were obtained (see **Figure 2(b)**). These results suggest that the overpotential at cathode would decrease with a decrease in the current density, as a result of this, the rate of nucleation become slower. Therefore, the current density is an important factor to control the particle size and density distribution.

The morphology and the particle size of the gold nanoparticles can also be modified by changing the electrodeposition time. El-Said and Fouad [25] deposited the gold nanoparticles on the ITO substrate by using electrolyte of an aqueous solution of 1 mM $HAuCl_4$. The authors observed that the particle size of the deposited gold nanoparticles increases with increasing the deposition time from 5 to 15 s, however, the morphology remains unchanged. On further increase of the deposition time to 20 s, a change in the morphology from nanospheres to the nanostars was observed. Again, the morphology of the nanostars remain unchanged for the deposition time

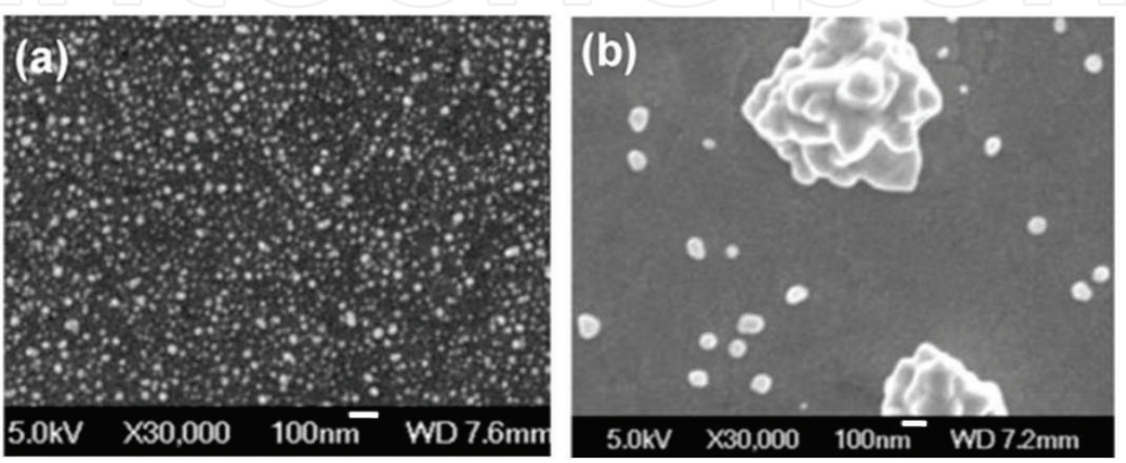

Figure 2.
SEM micrographs of gold nanoparticles deposited on the ITO glass substrate at (a) 11 mA/cm² and (b) 0.3 mA/cm² [24].

25 and 30 s, however, a slight increment in their diameters was observed. A similar type of variation in sizes of gold nanoparticles with respect to deposition time also reported by Sakai et al. [26]. Dependence of particle size on the deposition time can be explained as follows: (a) During the electrodeposition process, formation of nanoparticles starts by nucleation of nuclei on the substrate; (b) The rate of nucleation is faster at the beginning of electrodeposition process; (c) As electrodeposition process proceeds, growth of these nuclei take place; (d) After prolonged deposition time, the whole surface of the substrate is covered by gold nuclei, the rate of nucleation of new nuclei decreases at this stage; (e) After filling of the substrate surface from the nuclei, the growth of nuclei takes by the diffusion process.

5. Electrodeposition of one-dimensional gold nanostructures

Recently, one-dimensional metallic nanostructures such as nanorods, nanotubes, nanowires have received the considerable attention of material scientists due to their unique properties and exciting applications in the field of magnetic storages devices, optoelectronic, cooling system, etc. [27]. One-dimensional gold nanostructures can be synthesized by photolithography and template-based electrodeposition techniques. The photolithography technique is costly due to the high equipment cost, photoresist and developer consumption, high mask cost, etc. For the production of nanorods and nanotubes of different sizes, different masks are required which increase production cost. Despite high production cost, the photolithography technique has emerged as a widely known technique for the production of different sizes of one-dimensional nanostructures such as nanorods and nanotubes. Unlike of the photolithography technique, template-based electrodeposition technique is a simple approach to produce one-dimensional nanostructures in relatively lesser production cost. The porous aluminum oxide (AAO) membranes are most widely used as templates to produce nanostructures. The structure of AAO membrane is regular hexagonal arrays. **Figure 3** shows schematics of the formation of gold nanotubes in AAO membrane. As, it is clear from the schematic diagrams that the morphology of the nanotubes progressively changes from hollow nanotubes to the solid nanotubes with progress in deposition time. The change in the morphology of the nanostructures strongly depends on the electrodeposition process parameters. Template-based electrodeposition technique provides a good control over dimensions of the target, and it can be used to produce a wide range of materials with aligned structure [27].

In template-based electrodeposition technique, before starting the electrodeposition in the template, the template is pre-processed. A thin layer of the conductive layer is sputtered on the bottom side of the template. This conductive layer makes a bridge over the pores and pores remain open. After that, the template is soaked in the deionized water for a certain period by ultrasonication. After ultrasonication of the template, electrodeposition is performed on it.

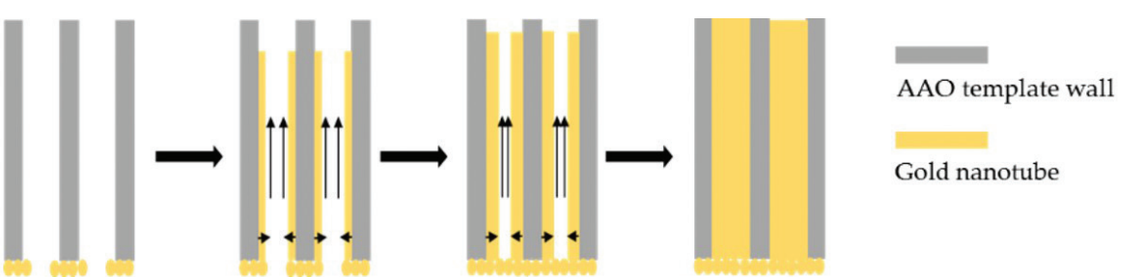

Figure 3.
A schematic diagram of the formation of gold nanotubes from hollow morphology to the solid morphology.

A lot of research has been dedicated to produce the gold nanotubes and nanorods. Wang et al. [27] produced the gold nanowires with tubular-rod structure by the electrodeposition process using the AAO membrane as a template. The average diameter of gold nanowires was about 180 nm and the average height was about 60 μm. The average diameter of the gold nanowires was found to be the same diameter as the average diameter of the pores of the template. To produce this nanostructure, a layer of the platinum on the bottom side of the AAO membrane template was deposited by the sputtering. The sputtering current was 45 mA and the deposition time was 150 s. For the electrodeposition of gold nanowires, chloride solution (5 g/L $HauCl_4 \bullet 3H_2O$, 2 g/L EDTA, 65 g/L Na_2SO_3, 12.5 g/L K_2HPO_4) was used and the deposition current density was 4.5 mA/cm^2. EDTA is a polyamino carboxylic acid and it acts as a chelating agent. Polycarbonate templates can also use for the production of gold nanotubes. Mollamahalle et al. [28] successfully electrodeposited gold nanotubes in polycarbonate templates with different lengths even as long as the template thickness (see **Figure 4**). But, for the electrodeposition of long gold nanostructures, the major problem found to be associated with polycarbonate template was the occurrence of blockage of the pores. To eliminate this problem, a coupling agent was used. The coupling agent 3-aminopropyltriethoxysilane (APS) was used to functionalize the pore walls of the template. By the ethoxy groups, the APS molecules are easily attached to the hydrophilic pore walls, while amino groups are faced in the electrolyte. Amino groups have a strong tendency to attract the gold ions which enhance the growth of deposit in the vertical direction of the pores by suppressing growth in the radial direction. A cyanide-based electrolyte was used for the deposition of these gold nanotubes. After electrodeposition of the gold nanotubes, the template was cleaned by using the deionized water to remove any residual impurities on the surface of it. Finally, the template was dissolved in a CH_2Cl_2 solution for 30 minutes to obtain gold nanotube for further characterization.

The length of the gold nanotubes can be controlled by the electrodeposition parameters such as the deposition time, deposition potential, deposition current density, and the electrolyte concentration. Yang et al. [29] studied the effect of the deposition potential and time on the morphology of gold nanotubes which was electrodeposited by using chloride solution in the AAO templates. Growth directions of the gold nanotubes were both along the length as well as along the thickness. However, the preferred growth direction was the thickness of gold nanotubes (see **Figure 3**). The morphology of the gold nanotubes was changed from hollow to solid nanotubes when the electrodeposition time proceeded. Tian et al. [9] reported the electrodeposition of rod-like gold nanostructures from a chloride solution (0.1 M $HClO_4$, 4–40 mM $HAuCl_4$) without using the template. The rod-like nanostructures (100 nm wide and 200–300 nm long) were obtained by applying the negative

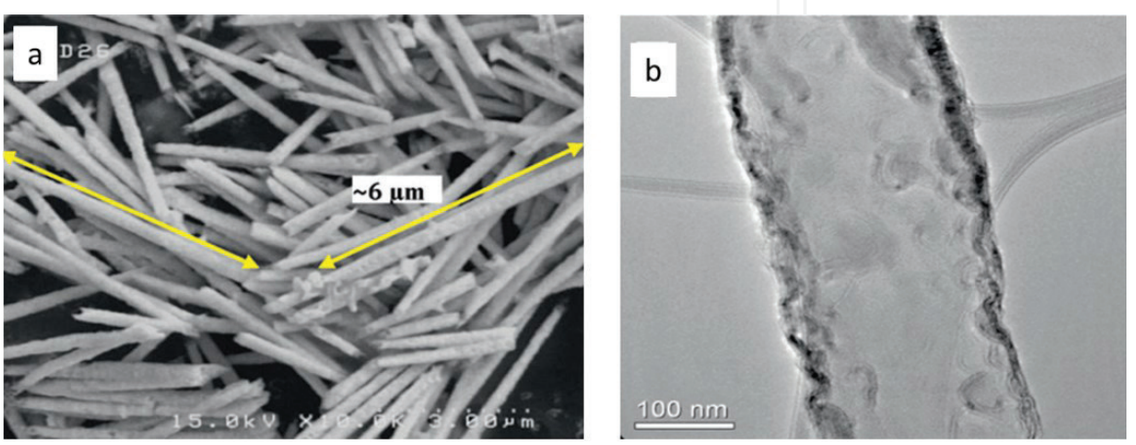

Figure 4.
(a) SEM micrograph of gold nanotubes and (b) TEM micrograph of individual gold nanotube [28].

potential of −0.08 V versus Ag/AgCl. The authors observed a change in morphology of rod-like nanostructure of the gold in changing the electrodeposition parameters such as electrolyte concentration and potential. The rod-like morphology was changed to nanopyramidal nanostructures (50–200 nm edge length at the bottom and several hundreds of nanometer in height) when the concentration of $HAuCl_4$ was increased from 4 mM to 40 mM. On the other hand, spherical nanostructure morphology (70–100 nm in diameter) was obtained when the potential increased from −8 to −2 V keeping the concentration of the $HAuCl_4$ at 40 mM.

6. Electrodeposition of two-dimensional gold nanostructures

In recent years, gold thin films have finds several technological applications in MEMS, optoelectronics, and electronics industries. To enhance the applicability and suitability of gold nanostructure films in the above-mentioned fields, modification of morphology of deposited nanostructure is required to achieve desired properties. Nowadays, there are wide varieties of a thin film of gold deposition methods based on high vacuum, such as sputtering [5], evaporation [6], molecular ion beam [7], and without vacuum such as electrodeposition [2, 4, 14], electroless deposition [30]. Among these methods, electrodeposition method has grown rapidly in recent years due to its time efficiency, cost-effectiveness, and absence of vacuum technology. In this method, the morphology of the deposited gold nanostructure film can also be easily controlled by varying the electrodeposition process parameters. Some of the crucial process parameters influencing the morphology of gold nanostructures films are discussed in given below sub-sections.

6.1 Cathode agitation

During the electrodeposition, the vicinity of mass in the electrolyte near the cathode surface takes place with deposition time. The vicinity of mass leads the poor quality of coating such as (a) phase change, (b) composition variation in coating across the thickness, (c) influence of the stress [12]. The mass transport in the electrodeposition process influences the properties of the coated films or layer [31]. This transport phenomenon could be controlled by the cathode agitation or electrolyte agitation. The cathode agitation can be achieved by the slider-crank mechanism while the electrolyte agitation is achieved by a magnetic stirrer. If the instantaneous linear velocity of the cathode agitation is sinusoidal, then the root mean square velocity of the crank is given by Eq. (4) [4].

$$v_{rms} \approx \frac{r\omega}{\sqrt{2}} \tag{4}$$

where v_{rms} is the root square velocity of the crank, r and ω are the radius and angular velocity of the crank, respectively. The cathode agitation affects the intrinsic stress in the coated gold film. Intrinsic stress decreases with increasing the agitation speed (v_{rms}) [4]. Therefore, cathode agitation could be used as a parameter to control the stress in the gold film.

6.2 Current density

Current density also plays a crucial role in the creation of stresses in the deposited gold film during the electrodeposition process. Pu et al. [4] studied the effect of the current densities on the stresses generated on the deposited gold film during the

electrodeposition process. They investigated this, at the range of current densities from 1.0 to 5.0 mA/cm^2. The electrolyte temperature and the film thickness were maintained at 55°C and 0.7 μm, respectively for each value of current density. The observed effects of current densities on the generated stresses of the deposited films are shown in **Figure 5**. The results showed that the deposited gold films have compressive stresses of range – 35 to 103 MPa within the range of deposition current densities from 1.0 to 5.0 mA/cm^2.

It is also reported in the scientific literature [32, 33] that the current density plays a very important role in the occurrence of a transition in growth mode of deposited nano-structured film. Furthermore, the generation of compressive stresses on the deposited gold film can also be evaluated on the basis of its growth mode and incorporation of impurities on it during the electrodeposition process [34, 35]. The adatom insertion into the grain boundaries and inclusion of impurities in the deposited film during the electrodeposition process together are the main suspected sources of generation of compressive stresses on it. However, the relative contribution of these two factors on the generation of compressive stresses on the deposited films is difficult to calculate.

In another study, reported by Kal et al. [2], it was observed that the deposited gold films have tensile stresses when the cyanide-based electrolyte is used. They studied the effect of current densities on the stresses of the deposited films at different annealing temperatures. The results obtained are shown in **Figure 6**. It is interesting to note that the observed trends in stresses with current densities are similar in natures at different annealing temperatures. However, the stresses are sufficiently high at relatively higher annealing temperatures. The result shows that at low current density, the tensile stress value is low and it increases with an increase in the current density till 4 mA/cm^2, after that it starts to decrease in the further increase in current density at different annealing temperatures. At higher annealing temperature, the grains of the deposited film re-arrange themselves with considerable growth in their sizes. While coming back to room temperature after the annealing, the film structure relaxes. As the thermal coefficient of expansion of the film and substrate is different, the substrate and the film cool down with a different rate that leads to the creation of tensile stresses in the film [36].

In both the results (**Figures 5** and **6**), the behavior of the observed stress with current densities are similar, but, the type of stresses generated in the films are different due to differences in employed electrolytes. Therefore, the nature of the

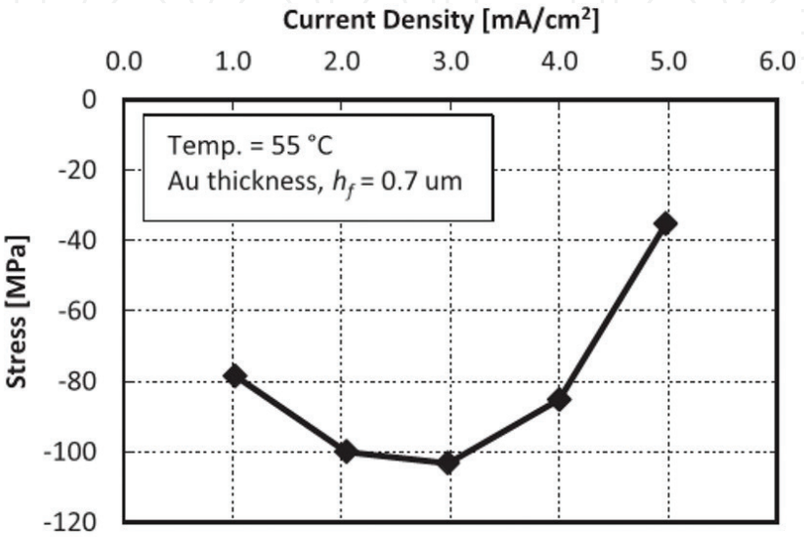

Figure 5.
Effect of current density on the stress of the Au-coated film [4].

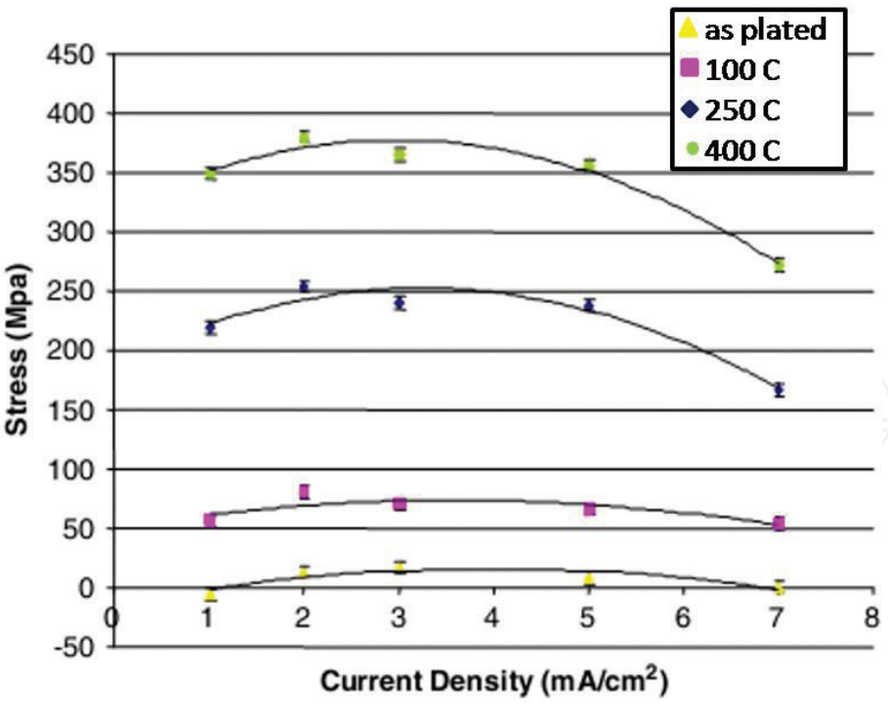

Figure 6.
Stress variation with current density at different annealing temperature [2].

generated stresses on the deposited films can be controlled by changing the current density and electrolyte.

The magnitude of generated residual stress in the gold film can also be controlled by adding the suitable stress-relieving additives in the electrolyte bath. Kelly et al. [17] studied the behaviors of stresses generated in the deposited films with and without adding stress-relieving additives in the electrolyte bath. It was observed that the films deposited without additives in the electrolyte bath had high tensile stresses within the range of 50–80 MPa at the current densities of the range of 1–4 mA/cm^2. However, with the addition of stress-relieving additive of 25 ppm arsenic ions in the electrolyte bath, the values of stresses in the deposited films were found to decrease with increasing current densities. In this case, at the current densities of the range of 1 to 4 mA/cm^2, the values of stresses generated in the films were within the range of −10 to −40 MPa,

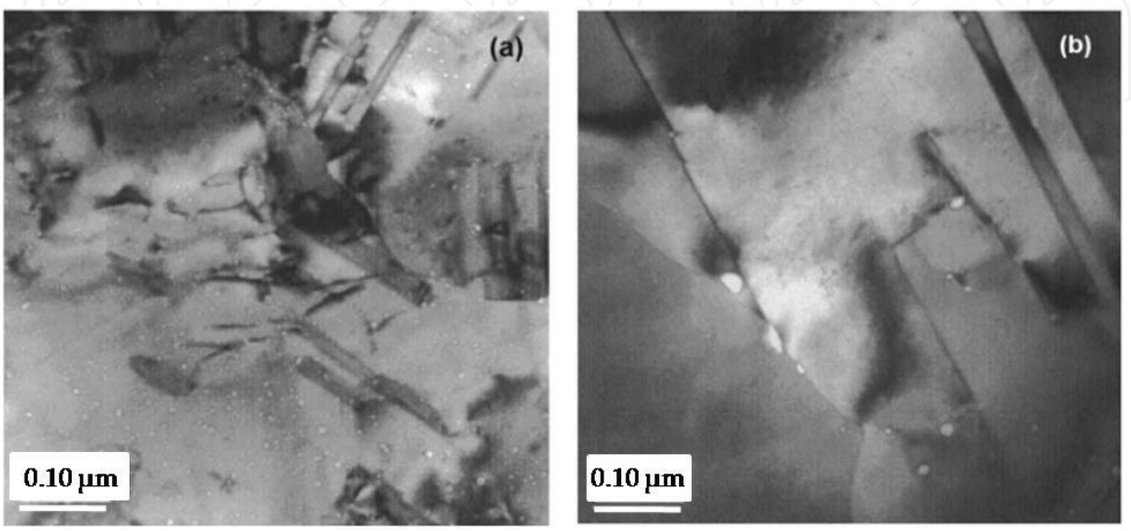

Figure 7.
Plan-view TEM-BF micrographs of gold films deposited at a current density value of 2 mA/cm². Micrographs (a) arsenic-free film and (b) 25 ppm arsenic-containing gold film [2].

respectively. **Figure 7** shows representative the bright field TEM micrographs of the gold film deposited at the current density 2 mA/cm^2 with and without arsenic content. As it is obvious from the TEM micrograph that the arsenic-free film reveals the presence of a high level of porosity (white tinny spots of nanometer range are believed to be nano-pores), twins, and dislocations with moderate (111) orientation. On the other side, the TEM micrograph of the arsenic-containing gold film reveals strong preferred (111) orientation with the relatively lower level of twins, dislocations, and pores. These results indicate that the observed microstructural change in the deposited gold films with and without stress-relieving additives in the electrolytic baths occurred due to their different growth modes which generate different levels of stresses in the final product.

6.3 Electrolyte temperature

The temperature of the electrolyte is also a very important parameter that influences the morphology of the deposited gold film. de Sá et al. [37] studied the effect of electrolytic temperature on the microstructural (morphological) evolution in the deposited gold films at a constant applied potential (−1 V) and a deposition time (1500 s). They employed pyrrolidinium-based ionic liquid electrolyte for the experiments. **Figure 8** shows SEM micrographs of deposited gold films that obtained at different temperatures (293, 333, and 353 K) of the electrolytes and a constant applied potential (−1 V) and deposition time (1500 s). As it is revealed by the micrographs that the continuity and the particle size in the deposited films increase with increasing temperatures of the electrolyte. At relatively higher electrolyte temperatures (333 and 353 K) the particles of deposited gold films were continuous,

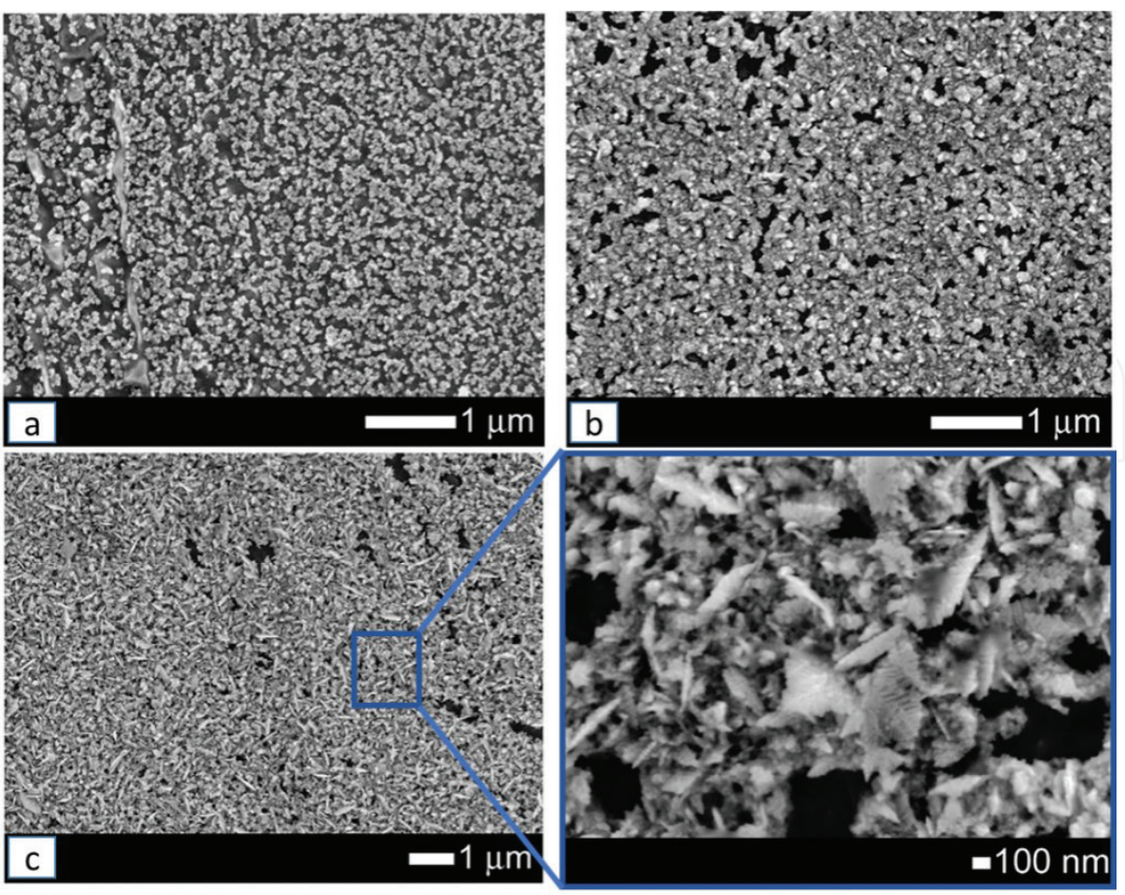

Figure 8.
SEM micrograph of gold films deposited at the potential of −1 V during 1500 s at different temperatures of (a) 293 K, (b) 333 K, and (c) 353 K [37].

while at a relatively lower temperature (293 K), the particles in the obtained gold film were discontinuous and poorly adherent with each other. Deposited films have acicular particles with a dendritic kind of morphology on the top surface of the globular film. At a relatively higher temperature of the electrolyte, the deposited film has large dendritic particles with well-developed primary and the secondary arms (see **Figure 8(c)**). The primary arms of the dendrites develop in <100> direction while the secondary arms in <111> directions [37, 38].

A similar type of morphology of the particles in the deposited film is also reported by Oyama et al. [39]. They deposited gold film by using an electrolyte solution of NaAuCl4/EMI-BF4, the deposition potential of −1 V, and the deposition time of 1000 s. The dendritic gold nanostructure could be grown by increasing the deposition time. The formation of dendritic morphology of the gold nanostructure could be attributed to the prolonged deposition time. The formation mechanism of dendritic nanostructures can be explained by the anisotropic crystal growth and diffusion-limited aggregation (DLA) model [40, 41]. This model says that in the electrodeposition process of the gold nanostructure films on the substrate, initially Au^{3+} ions in the electrolyte rapidly reduces and forms the gold adatom. As deposition proceeds, a large number of gold nuclei accumulates on the surface of the substrate and further grow to form nanoparticles of the gold. These gold nanoparticles hit and stick to each other and form a growth core. The gold nanoparticles accumulate continuously on the growth core and form a backbone of the dendrites after sufficiently large deposition time. As the deposition time becomes prolonged, the concentration of gold salt in the electrolyte decreases. This leads to the formation of new gold nanoparticles which attaches to the surfaces of the dendritic backbone. This oriented attachment of gold nanoparticles in the dendritic backbone looks like new shorter branches [42].

7. Conclusions

In this chapter, an overview of the morphology controlled synthesis of zero-dimensional, one-dimensional, and two-dimensional gold nanostructures by electrodeposition techniques are discussed and presented. Furthermore, the information related to effects of the electrodeposition process parameters (such as current density, deposition time, concentration and nature of electrolyte) in the morphologies of nanostructured gold deposits are provided in detail. Based on the observations of above discussed experimental works of the electrodeposition of the nanostructured gold reported by different groups of researcher the following general conclusions can be drawn.

1. The properties of the electrodeposited nanostructured gold can be simply controlled by tuning its morphology. And, the morphology of the deposited gold can be tuned by changing the electrodeposition process parameters (such as current density, composition, and pH of the electrolyte, addition of suitable additives in the electrolyte, temperature of electrolyte, etc.).

2. The morphologies of the nanostructures gold strongly depend on the nature of the electrolytes used for the electrodeposition process. A cyanide and a noncyanide based electrolyte are found to be suitable for the deposition of the nanostructured gold of different morphologies. The problem associated with the cyanide-based electrolyte is its toxicity and incompatibility with positive photoresist. These problems can be eliminated by replacing cyanide-based electrolyte with an alternative noncynide-based electrolyte.

3. The morphology and the size of the electrodeposited gold nanoparticles can be controlled by the applied current density and the electrodeposition time.

The particle size of the deposited gold decreases and their density increases with increasing the current density. The particle size of the deposited film also increased with increasing the temperature of the electrolyte. At relatively prolonged deposition time, the growth of the well-developed dendritic kind of morphology in the deposited gold nanostructured film is favored. The lengths and morphologies of the one-dimensional gold deposit such as nanotubes can also be controlled by the deposition time. The length of the nanotubes increases with increasing deposition time. At prolonged electrodeposition time, the morphology of the gold nanotubes changes from hollow to solid nanotubes. The morphology of the one-dimensional nanotubes also changes with changing the concentration of the electrolyte.

4. The stress generated in the gold deposit is unwanted for their application. The generated stresses in the gold deposit can be controlled by the applied current density, nature of the used electrolyte, cathode or electrolyte agitation and post-deposition annealing treatments. The internal stresses increase with increasing the current density, and above the certain current density, the internal stresses start to decrease. The internal stresses in the deposited structures can be minimized by the application of agitation of the electrolyte. The internal stresses reduce with increasing the speed of agitation of the electrolyte by a magnetic stirrer. Also, the stresses in the deposited film can be decreased by post-deposition annealing of the film at a relatively lower temperature. Furthermore, the stresses in the deposit can also be minimized by adding some suitable additives such as arsenic ions in the electrolyte.

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